

***Pteridium caudatum* (L.) Maxon Behaves as a Potassium Plant and Accumulates Aluminum in the Subterranean Organs**

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ABSTRACT.—The purpose of this study was to investigate the nutritional status of *Pteridium caudatum* (bracken fern) in a Neotropical region where this species occurs in acid leached soils. In this region there is a high availability of Al in soluble toxic forms, rendering *P. caudatum* an important weed associated with wildfire regimes. Water-soluble Ca, exchangeable Ca fraction, Ca bound to pectate + phosphate, and bound to oxalate were evaluated from *P. caudatum* sampled from a burned parcel of land 94 and 270 days after an accidental fire, as well as from an unburned control parcel. Both sites were located in a tropical secondary savanna community in a successional mosaic of a cloud forest. The concentrations of total Ca, N, P, K, Mg, Fe, Mn, Zn, Cu, Ni and Al, and their distribution in the plant organs were investigated. The study addressed the hypothesis that shoots should show low concentrations of Ca because a low cation capacity exchange has been reported in roots of *Pteridium*. We expected a low water-soluble Ca fraction because bracken has been defined in the literature as a non-calcicole plant. The exchangeable fraction and pectate + phosphate bound Ca constituted 60 to 85% of the total Ca in pinnae and rhizomes, while the oxalate bound Ca constituted only 3 to 14% of the total Ca. Concentrations of Al as high as 248.3 mmol kg⁻¹ were found in roots. Pinnae showed only 84.53 mmol Ca kg⁻¹ and 5.62 mmol Al kg⁻¹, and their Ca/Al ratio was 15 mol mol⁻¹ contrasting with *P. aquilinum* from temperate regions where Ca/Al was 1440 mol mol⁻¹, however the Ca/P was 2 mol mol⁻¹ in both species. We conclude that *P. caudatum* behaves as a potassium plant (soluble K/Ca >>1) such as the grass-like families Poaceae and Cyperaceae and accumulates Al in the subterranean organs.

Bracken ferns of the world-wide genus *Pteridium* appear in the Neotropics on land exposed to human intervention where primary cloud forests have been converted into montane savannas (Alonso-Amelot and Rodolfo-Baechler, 1996). The basic characteristics of tropical montane cloud forests are that they capture water from clouds, have low evapotranspiration rates and add water to the hydrologic system. These forests are threatened by anthropogenic fire usually associated with grazing, agricultural interventions and hunting (Hamilton *et al.*, 1995). *Pteridium* occurs especially widely in fire burned habitats and, unusually, has the ability to pioneer ash-burn surfaces of high potash levels and highly alkaline pH, metamorphosing to become an acidophilus plant once its rhizomes penetrate beyond the initial ash surface layers (Page, 2004).

It is important to understand the mineral nutrition of bracken because this perennial weed causes problems for agriculture, forestry, conservation and

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animal health, despite many attempts to develop control strategies (Papavasiliou, 2003). The nutritional status of *Pteridium aquilinum* (L.) Kuhn has been studied in temperate climates (Thompson *et al.*, 1997; Skre *et al.*, 1998) and there are several studies of the Neotropical bracken fern, *P. caudatum* (L.) Maxon, concerning xenobiotic materials such as phenolics, tannins, the cyanogenic glycoside prunasin, and illudanes, which protect the plant from herbivores (Alonso-Amelot and Avendaño, 2002; Alonso-Amelot *et al.*, 2001; 2004). However, as far as we know, bracken's nutritional status in tropical environments has not been investigated.

There is variation in the shoot Ca content of angiosperms (Broadley *et al.*, 2003), the lowest values corresponding to orders of commelinoid monocots (rice, cereals, maize, bananas). According to Broadley *et al.* (2003) root cation-exchange capacity (CEC), pectin and Ca shoot content may be correlated. We expect a lower Ca content in bracken than in dicots based on the low CEC found by Koedam *et al.* (1992) in *P. aquilinum* roots. The root CEC is located in the apoplast and is attributed to the free carboxyl groups of galacturonic acids of cell wall pectins in the middle lamella. The pectin contents of shoot cell walls are comparable to those of root cell walls (Broadley *et al.*, 2003).

According to White and Broadley (2003) plants with a low soluble Ca concentration include the potassium plants, characterized by high shoot K/Ca quotients, and the oxalate plants, which have high tissue oxalate concentrations. Plants that accumulate oxalate can be subdivided into species that contain soluble oxalate and those in which Ca-oxalate is precipitated. Iljin in 1936–1944 (Kinzel, 1983) designated the term calciotropic to plants which contain appreciable amounts of water-soluble Ca. This physiological terminology refers only to Ca metabolism and is different from the geobotanical label calcicole, which refers to the flora observed on calcareous soils. In such a flora, nutrient acquisition and ecological success depend not only on Ca, but also on other factors such as their root development, microorganism associations, rhizosphere pH, root exudates, etc.

The three distinct physiotypes for Ca nutrition, potassium plants, oxalate plants and calciotropes, are characteristic of particular angiosperm families (White, 2005), therefore it is interesting to investigate the K/Ca ratio and the total Ca fractionation in a fern. In acid soils of the Instituto Venezolano de Investigaciones Científicas (IVIC) calciotropes, such as *Clusia multiflora*, are present with a total Ca concentration of 244 mmol kg⁻¹, and water-soluble Ca representing 77% of the total Ca, while oxalate comprises only 6% of the total, but this species is also found in dry calcareous forests where it was found to have Ca concentrations of 403 mmol kg⁻¹ (Olivares and Aguiar, 1999). Bracken has been defined as an acidiphilous pteridophyte (Koedam *et al.*, 1992; Page, 2004); it usually does not grow on calcareous soils and we may expect a low water-soluble Ca fraction because this fraction is advantageous as an osmotic counter ion in xerophytic, calcareous environments, which is the opposite of bracken habitat. Therefore bracken is predicted to have the physiotype of a potassium or oxalate plant. The Ca physiotype of plants is genetically determined and phylogenetic information has been used to identify crops with

higher Ca content to address Ca malnutrition in humans (White, 2005). It can also be useful to identify if the weed shows a high oxalate fraction and is able to survive excessive Ca in calcareous soils and under liming, or if it behaves as plants in the Poales with a high K/Ca due to lower requirements of Ca than dicots.

In the present study we sampled *P. caudatum* in a tropical secondary savanna community in Venezuela, in a site where tropical montane cloud forest has given way in some areas to secondary savannas due to recurrent human-related fires in the last two centuries. The site is characterized by acid soils (García-Miragaya and Herrera, 1971; Marulanda, 1998). The objectives of this study are: 1) To measure Ca concentrations in pinnae and rhizomes of *P. caudatum* three and nine months after an accidental fire, in May and November, and to contrast these data with control plants growing in a unburned parcel. We expect higher Ca in burned parcels due to the effect of ash fertilization. Similar values of Ca in plants from burned and control parcels will indicate leaching of nutrients during the experimental time. 2) To compare the shoot Ca concentration in the pteridophyte with monocots and dicots reported in the literature, considering that remarkable differences have been found probably as a consequence of their different CEC and pectin contents in the cell wall. 3) To define the physiotype by the soluble K/Ca ratio, related it to its acidiphily, and to evaluate the proportion of soluble, exchangeable pectate + phosphate and Ca-oxalate. 4) To evaluate the distribution of mineral elements in the plant organs.

MATERIALS AND METHODS

Plant material and field sampling.—*Pteridium caudatum* [= *Pteridium aquilinum* var. *caudatum* (L.) Domin], supported in the specific rank by Thomson and Alonso-Amelot (2002), was sampled within the grounds of the Instituto Venezolano de Investigaciones Científicas (IVIC), located in Altos de Pipe (10° 24'N, 66° 58'W, 1380 m above sea level). The predominant vegetation at IVIC is primary cloud forest, surrounded by secondary forests and grasslands. Occasionally fires take place during the dry season in the secondary vegetation units. Disturbed areas between the forest and grassland are dominated by ferns. The plants were sampled in a tropical secondary savanna community. The 10-yr average annual precipitation of 1100 mm is relatively well distributed throughout the year, with only two months (February and March) of dry season (Sanhueza *et al.*, 2000). The study was performed in the rainy season (May and November). Soil profiles from Altos de Pipe showed a water pH of 4.7 to 5.2 (García-Miragaya and Herrera, 1971).

Five relatively small plants (< 0.3 m tall) and five larger plants (> 1 m tall), denoted as *s* or *l*, respectively, were collected in a burned parcel (B) in May and November 94 and 270 days after an accidental fire that occurred on February 14, 2003. Sampling was also carried out in a control parcel (C) where fire did not take place. Plants are defined here as fronds and attached underground parts excavated from holes 50 × 50 × 20 cm. Small and large

plants were present in the second sampling in November, but small plants were not found in May in the control parcel. This indicated that vegetative sprouting after May in the control parcel can be attributed to the fact that there were no monitored disturbances of this region. This is different from the fire burned region in which, presumably, there had been activity of small wild herbivores or humans, such as walking or clearing. The area of each parcel was approximately 400 m² and they were separated from each other by 1 Km. The distance between the samplings was at least 5 m. Sporophytes were sterile at both harvest times and had fronds with three to nine pinnae. The excavated plants were transported to the laboratory and the underground organs were washed with tap water. Aerial and underground organs were dried to constant weight in a ventilated oven for approximately 78 h at 60° C and then ground with a Wiley mill (3383-L10, Thomas Scientific, U.S.A.). The aerial biomass, given by the dry mass of pinnae (green tissue) and rachis + petioles was measured. The total biomass was not calculated because we were not sure if we collected the entire rhizome length in the explored soil area (50 × 50 × 20 cm). Mineral analysis in aerial and underground organs was performed and expressed by dry mass.

Chemical analyses.—The Ca fractionation methodology of Kostytschew and Berg described in Kinzel (1989) was used: Hot water-soluble Ca, originally included in the vacuoles, was obtained by heating ground plant material in a proportion of 200 mg dry mass to 5 mL water. After centrifugation at 4.6 G for 10 min, the liquid was collected and the residue treated with the next extracting solution. Calcium adsorbed electrostatically on the cell walls or on polyanions in the vacuoles was extracted by means of hot 10% NaCl solution. The Ca-phosphate + pectate fraction was extracted by means of hot acetic acid (2 mM). In each case the extraction mixture was heated to the boiling point of the solution. Finally, Ca bound to oxalate was extracted overnight with HCl (2 mM) at ambient temperature. The extraction efficiency, calculated by the linear regression of the sum of fractions versus the total Ca, was 95%.

The soluble K in hot water extracts was measured and the K/Ca ratio in pinnae and rhizomes was calculated. The concentration of Ca and K in the water extract and Ca in other extracts were determined on an atomic absorption spectrometer (SpectrAA 55B, Varian Techtron, Victoria, Australia). Rhizomes were used instead of roots for the fractionation because the dry mass of roots per plant was too small for analysis, but concentrations of total Ca, K, Mg, Fe, Al, Mn, Ni, Zn and Cu, were determined from all the organs in nitric-perchloric acid digestions (Miller, 1998).

Total nitrogen concentration was determined by the Kjeldhal method (Tecator Kjeltex Systems from Foss Tecator, Höganäs, Sweden) after digestion of the ground dry plant material with sulfuric acid. Phosphorus was measured colorimetrically (Murphy and Riley, 1962) in the digested material by means of UV/visible spectrophotometer (Ultrospec 2000, Amersham Pharmacia, Cambridge, England). Ash content was determined by heating biomass samples to 510 °C for 8 hours in a muffle furnace (Thermolyne, Iowa, U.S.A.).

Molar ratios (mol N/mol P) for the mineral elements instead of mass ratios (g N/g P) are shown in the present work because they are more common in physiological research, as they reflect the actual stoichiometric relationships. They differ by a factor of 2.21. For comparative purposes mass ratios, common in the literature, were recalculated to molar ratios.

Statistical analysis.—Standard errors are used as indicators of sampling error rather than treatment effects. The values from the seven categories shown in Table 1 (May-Bs, Bl, Cl and November-Bs, Bl, Cs, Cl) were pooled to get the average shown in Table 2. For aerial organs and rhizomes chemical analyses were duplicated ($5 \text{ plants} \times 7 \text{ categories} \times 2 \text{ chemical analyses} = 70$), but for roots the dry mass was insufficient for replicate chemical analyses ($n = 35$).

RESULTS

Total Ca concentration in P. caudatum of different size and fire history.—A clear difference in total Ca concentrations between plants of different size from the burned and control parcels was not observed. Calcium concentration in pinnae was higher than that measured in rhizomes and the highest Ca concentration was found in plants from the control parcel sampled in May (Table 1).

Ca fractionation and soluble K/Ca ratio.—The exchangeable fraction represented up to 62% of the total Ca in rhizomes from small plants and up to 53% in the pectate + phosphate fraction in pinnae from large plants, both sampled in the burned parcel in November (Table 1). The exchangeable and phosphate + pectate fractions taken together contributed 60 to 85% of the total Ca in pinnae and rhizomes. The exchangeable fraction was higher than, or nearly equal to, the pectate + phosphate fraction, except in pinnae from the burned parcel in November. The same pattern of low oxalate-Ca was found in pinnae and rhizomes. Water-soluble Ca contributed to the total Ca in a lower proportion in rhizomes than in pinnae and the highest value of this fraction was 28% in pinnae from small plants from the burned plot in November. Pinnae had higher soluble K concentrations than rhizomes. The highest concentration of soluble K and K/Ca ratio were found in pinnae from the burned parcel.

Biomass, N, P and ash content in P. caudatum of different size and fire history.—Aerial biomass appears to be higher in non-burned plots samples (Table 2). The highest value of ash content in *P. caudatum* was found in rhizomes. Pinnae from burned and control parcels were similar in ash content, but rhizomes from the burned parcel showed a higher ash percent of dry mass. Contents of P were higher in burned plot samples of pinnae and rhizomes. Large plants sampled in May in the non-burned plot had the lowest contents of N and P found in this work for pinnae.

Distribution of metals in the plant organs and ratio of total mineral elements in pinnae.—Underground organs showed higher concentrations of Al, Fe, Zn, Cu and Ni than aerial ones, and roots showed higher concentrations of these metals than the rhizomes (Table 3). The concentration of Mn was higher in

TABLE 1. Total Ca concentration and fractions of Ca, expressed in per cent of total, extracted with hot water (water-soluble), hot NaCl solution (exchangeable), hot acetic acid (Ca-phosphate and Ca-pectate) and HCl (Ca-oxalate), water-soluble K and soluble K/Ca ratio in relatively small (s) and larger (l) *P. caudatum* from a burned (B) field, 94 and 270 days after fire, and from a control (C) plot. For each category values given are means \pm SE (n = 5).

	Calcium						
	total	water-soluble	hot NaCl	hot acetic	HCl	Sol. K	Sol. K/Ca
	mmol kg ⁻¹	(% total Ca)				mmol kg ⁻¹	mol mol ⁻¹
PINNAE							
May, 94 days after fire							
Bs	54 ± 12	16	42	34	8	431 ± 38	101 ± 22
Bl	80 ± 6	18	36	38	8	419 ± 29	41 ± 6
Cl	116 ± 9	18	48	29	5	309 ± 37	22 ± 2
November, 270 days after fire							
Bs	101 ± 12	28	23	37	12	514 ± 92	37 ± 17
Bl	59 ± 4	21	23	53	3	740 ± 41	83 ± 21
Cs	110 ± 12	22	50	21	6	269 ± 20	13 ± 2
Cl	71 ± 10	13	52	27	9	260 ± 20	44 ± 15
Burned (n = 20)	73 ± 6	21 ± 3	31 ± 5	40 ± 4	8 ± 2	532 ± 35	67 ± 10
Control (n = 15)	99 ± 7	18 ± 3	50 ± 1	26 ± 2	6 ± 1	279 ± 16	26 ± 5
RHIZOMES							
May							
Bs	49 ± 6	18	46	27	9	273 ± 20	29 ± 5
Bl	35 ± 3	17	44	29	10	217 ± 16	31 ± 3
Cl	30 ± 4	12	51	24	14	202 ± 9	42 ± 3
November							
Bs	40 ± 3	6	62	24	9	75 ± 10	33 ± 4
Bl	26 ± 3	7	53	30	10	111 ± 8	63 ± 5
Cs	32 ± 2	10	38	43	9	163 ± 16	40 ± 4
Cl	25 ± 2	13	46	32	9	144 ± 10	43 ± 6
Burned (n = 20)	37 ± 3	12 ± 3	51 ± 4	28 ± 1	9 ± 0	167 ± 15	39 ± 3
Control (n = 15)	29 ± 2	12 ± 1	45 ± 4	33 ± 6	11 ± 1	170 ± 8	42 ± 3

rachis + petioles and rhizomes than in pinnae and roots. The quotients calculated with the average of the element concentrations in shoots are given in Table 3 for comparison with the literature.

DISCUSSION

Total Ca concentration in P. caudatum of different size and fire history.—The highest Ca concentration was found in large plants from the control parcel (116 \pm 9 mmol kg⁻¹; Table 1) which is low compared with the range (25 to 1249 mmol kg⁻¹) found in higher plants (Marschner, 1995). Thompson *et al.* (1997) found a Ca concentration of 142 mmol kg⁻¹ in pinnae of *P. aquilinum* in England (Table 3). In adult dry leaves of tropical plants, values of up to 955 mmol kg⁻¹ Ca have been reported (Olivares and Aguiar, 1999). Zohlen and

TABLE 2. Aerial (pinnae + rachis) and rhizomes biomass. The pinnae contribution in the aerial biomass is indicated. Total N and P concentration and ash content in the same plants of Table 1.

	Biomass (g dry mass plant ⁻¹)	Pinnae %	N (mmol kg ⁻¹)	P (mmol kg ⁻¹)	Ash (% dry mass)
PINNAE					
May					
Bs	8 ± 2	58	1646 ± 149	53 ± 8	6.9 ± 0.2
Bl	59 ± 6	77	1260 ± 51	24 ± 3	5.9 ± 0.4
Cl	52 ± 7	82	899 ± 27	4 ± 1	5.5 ± 0.8
November					
Bs	32 ± 4	70	1395 ± 118	49 ± 11	8.7 ± 0.9
Bl	62 ± 9	68	1369 ± 19	61 ± 4	6.7 ± 0.2
Cs	36 ± 7	88	1590 ± 57	33 ± 3	8.0 ± 0.9
Cl	91 ± 12	84	1439 ± 76	35 ± 6	5.7 ± 0.2
Burned (n = 20)	40 ± 13	68 ± 4	1425 ± 77	47 ± 8	7.1 ± 0.4
Control (n = 15)	60 ± 16	85 ± 2	1309 ± 210	24 ± 10	6.4 ± 0.5
RHIZOMES					
May					
Bs	13 ± 1		274 ± 28	12 ± 2	15.2 ± 3.0
Bl	9 ± 2		316 ± 16	10 ± 1	10.9 ± 0.9
Cl	11 ± 2		296 ± 20	9 ± 1	7.5 ± 0.5
November					
Bs	9 ± 2		431 ± 27	16 ± 4	10.3 ± 1.9
Bl	7 ± 3		363 ± 33	13 ± 2	5.5 ± 0.6
Cs	5 ± 1		603 ± 21	10 ± 2	9.2 ± 0.7
Cl	8 ± 1		432 ± 30	5 ± 1	6.8 ± 1.7
Burned (n = 20)	10 ± 1		346 ± 34	13 ± 1	10.5 ± 1.2
Control (n = 15)	8 ± 2		444 ± 89	8 ± 2	7.8 ± 0.6

Tyler (2004) reported 179 to 299 mmol kg⁻¹ Ca in calcifuge herbs from Sweden growing on acid soils, and 74 to 142 mmol kg⁻¹ Ca in calcifuge grasses. Monocots of the Poaceae take up less Ca than dicots for adequate growth and bracken also shows low Ca.

Ecologists have classified plant species into calcifuges, which occur on acid soils with low Ca, and calcicoles, which grow on calcareous soil (White and Broadley, 2003). The terminology was introduced by Chodat in 1913 and Salisbury in 1920 respectively (Kinzel, 1983). The response of calcifuges to acidic and calcareous soils is important in understanding their ability to compete and survive (Zohlen and Tyler, 2004) because calcifuge plants have a low capacity to solubilize soil P and this is related to low root exudation rates of di- and tricarboxylic organic acids, in particular oxalic acid. Phosphate in plant tissues may also be immobilized when calcifuge plants are forced to grow on a calcareous soil. Under such conditions an excessive uptake of Ca may take place in calcifuges, causing precipitation of Ca-phosphate in their tissues. Zohlen and Tyler (2004) reported calcifuge herbs not only have lower concentrations of soluble inorganic and total P in their leaves compared with calcicoles, but also a lower relative proportion of soluble P when grown on

TABLE 3. Mineral element concentrations in organs of *P. caudatum* (mean \pm SE): pinnae, rachis + petioles, rhizomes and roots (n = 35), compared with pinnae of *P. aquilinum* (n = 30) from Thompson *et al.* (1997).

<i>P. caudatum</i>					<i>P. aquilinum</i> ^a		
	Pinnae	Rachis+petioles	Rhizomes	Roots	Pinnae	<i>P. caudatum</i> <i>P. aquilinum</i> ^a	
Element (mmol kg ⁻¹)						Quotients in pinnae (mol mol ⁻¹)	
N	1374.49 (\pm 41.64)	458.11 (\pm 16.75)	389.97 (\pm 15.98)	527.92 (\pm 24.45)	2084.67 (\pm 16.94)	N/P	37 24
P	37.41 (\pm 2.84)	11.45 (\pm 1.05)	10.71 (\pm 0.68)	7.47 (\pm 0.89)	87.17 (\pm 1.18)	Ca/P	2 2
K	384.90 (\pm 14.94)	244.22 (\pm 17.03)	155.44 (\pm 6.40)	65.00 (\pm 9.83)	555.02 (\pm 4.67)	Ca/Mg	1 1
Ca	84.53 (\pm 4.58)	24.27 (\pm 1.45)	33.71 (\pm 1.70)	57.94 (\pm 5.02)	142.22 (\pm 1.82)	K/Ca	5 4
Mg	73.39 (\pm 2.31)	21.09 (\pm 1.61)	33.73 (\pm 2.04)	24.62 (\pm 2.78)	98.75 (\pm 0.75)	Ca/Al	15 1440
Fe	2.17 (\pm 0.25)	0.95 (\pm 0.16)	15.41 (\pm 1.26)	49.54 (\pm 7.02)	3.58 (\pm 0.03)	Al/Fe	3 0.03
Al	5.62 (\pm 0.49)	1.59 (\pm 0.17)	65.94 (\pm 5.51)	248.30 (\pm 28.95)	0.10 (\pm 0.00)	Fe/Mn	3 1
Mn	0.85 (\pm 0.08)	3.08 (\pm 0.32)	1.18 (\pm 0.08)	1.48 (\pm 0.29)	4.00 (\pm 0.13)	Mn/Zn	7 28
Ni	0.06 (\pm 0.01)	0.03 (\pm 0.00)	0.09 (\pm 0.01)	0.11 (\pm 0.02)	nd	Mn/Cu	12 7
Zn	0.13 (\pm 0.01)	0.04 (\pm 0.01)	0.07 (\pm 0.01)	0.96 (\pm 0.11)	0.14 (\pm 0.00)	Mn/Ni	14 nd
Cu	0.07 (\pm 0.01)	0.04 (\pm 0.00)	0.05 (\pm 0.01)	0.14 (\pm 0.04)	0.56 (\pm 0.00)		

^aMineral element concentrations in *P. aquilinum* from Thompson *et al.* (1997), in <http://www.shef.ac.uk/uni/academic/N-Q/nuocpe/ucpe/nutrient.txt>, were recalculated from mass to molar units.

a calcareous soil. This is of importance to their photosynthesis, growth, competition and final survival. Koedam *et al.* (1992) found that the soil preference with respect to soil acidity in *P. aquilinum* sampled in forests from Belgium, France, Luxemburg and Germany was in the acidic range (median pH 4.00) and they did not detect calcium carbonate in the substrate, therefore they considered bracken not to be a calcicole and it was labeled as acidiphilous.

Ca fractionation and soluble K/Ca ratio.—In *P. caudatum* the exchangeable fraction is the largest of the Ca fractions, and the pectate + phosphate fraction is also high (Table 1). This is similar to plants in the Boraginaceae in which NaCl and acetic acid extracts represented 56 to 68% of the total Ca (Kinzel, 1989). These fractions are in contrast to those of the calciotrophes in Brassicaceae with 49 to 66% of the total Ca in the water-soluble fraction, or with the oxalate plant, *Ballota nigra* (Lamiaceae), with 91% in the oxalate fraction (Kinzel, 1989). The physiotype of *P. caudatum* does not correspond to a calciotrophe according to the soluble K/Ca ratio (Table 1) nor to oxalate plants as they showed a low acid soluble fraction (Table 1). Therefore, the species behaves as a potassium plant, but with K soluble concentrations $<740 \pm 41 \text{ mmol kg}^{-1}$, which are lower values than those found in typical potassium plants such as *Carex pendula* (Poales) with soluble K concentrations $<2000 \text{ mmol kg}^{-1}$ (White, 2005).

Biomass, N, P and ash content in P. caudatum of different size and fire history.—When biomass data from Table 2 are recalculated by area units, the aerial biomass from plants in the burned parcel is $161 \pm 51 \text{ g m}^{-2}$ contrasting with $239 \pm 65 \text{ g m}^{-2}$ in control parcels, however rhizomes have similar biomass in both parcels, 36 ± 3 and $32 \pm 7 \text{ g m}^{-2}$, respectively. We only sampled to a depth of 20 cm and therefore failed to collect the complete rhizome. Alonso-Amelot and Rodulfo-Baechler (1996) reported 53 g m^{-2} and 143 g m^{-2} in fronds and rhizomes of *P. caudatum* in Venezuela.

Ash content in rhizomes of *P. caudatum* was higher than in pinnae, and was similar to that found by Skre *et al.* (1998), who found a maximum ash percentage of 7.2 ± 1.1 in non-green plant tissue of *P. aquilinum* plants from a burned parcel, contrasting with a lower value of 3.7 ± 0.5 in plants from an unburned site. However, they reported that the ash percentage of green leaves from a burned parcel and a control site were similar.

The concentration of P in shoots of *P. caudatum* was 4 to 61 mmol kg^{-1} , which is low compared with the range (3 to 194 mmol kg^{-1}) found in higher plants (Wright *et al.*, 2004). The concentration of N in shoots was 899 to 1646 mmol kg^{-1} , and the range found in higher plants is 143 to 4569 mmol kg^{-1} (Wright *et al.*, 2004). Thompson *et al.* (1997) found a P and N concentration of 87 mmol kg^{-1} and 2085 mmol kg^{-1} respectively in pinnae of *P. aquilinum* in England. Differences in N and P in burned and non-burned samples are not clear. Skre *et al.* (1998) reported that the P contents of green parts of *P. aquilinum* from a burned parcel and a control site in Norway did not show significant differences, $284 \pm 58 \text{ mmol kg}^{-1}$ and $258 \pm 45 \text{ mmol kg}^{-1}$,

respectively. The same was observed for N, $1785 \pm 428 \text{ mmol kg}^{-1}$ and $1499 \pm 214 \text{ mmol kg}^{-1}$.

Distribution of metals in the plant organs and ratio of total mineral elements in pinnae.—Very high concentrations of Al and Fe were found in underground organs compared to aerial organs (Table 3). Johnson-Maynard *et al.* (1997) reported a lower pH and higher exchangeable Al in a site invaded for 30 years by bracken fern than in an undisturbed forest and suggested that the establishment of bracken fern is responsible for the subsequent alteration of soil properties, which can have significant implications for the growth of other species. Higher organic C and a repartitioning of secondary Al and Fe from inorganic compounds into organic complexes characterize soils supporting bracken fern.

The high N/P ratios in *P. caudatum* (Table 3) may suggest a P-limited biomass production; however, fertilization experiments are necessary to confirm this hypothesis. Güsewell (2004) studied the variation and functional significance of N/P ratios in terrestrial plants and reported that often, but not always, N/P ratios <22 and $>44 \text{ mol mol}^{-1}$ correspond to N- and P- limited biomass production. Intraspecific variation was reported to be more important than interspecific variation, with N/P ratio variation of individual species of fifty-fold in response to natural or experimental variations in N and P supply. Han *et al.* (2005) found that higher N and P concentrations occurred in seed plants than in ferns, suggesting that these phylogenetic groups differed in leaf chemistry. Thompson *et al.* (1997) reported higher P and N concentrations and lower N/P ratio in *P. aquilinum* (Table 3) than found here for *P. caudatum* growing in acid soil. Han *et al.* (2005) studied *P. aquilinum* in China and reported 914 mmol kg^{-1} N, 27 mmol kg^{-1} P and an N/P ratio of 34 mol mol^{-1} .

The Ca/P quotient found in shoots of *P. caudatum* was 2 mol mol^{-1} (Table 3). Zohlen and Tyler (2004) reported a Ca/P ratio of 2 - 8 mol mol^{-1} in grasses, which is lower than that found in herbs ($4\text{--}51 \text{ mol mol}^{-1}$). They found the highest value of Ca/P in calcifuge herbs in calcareous soils. Calcifuge herbs with low oxalate exudation by roots and low oxalate precipitation in their tissues may not be able to survive calcareous conditions because of the precipitation of phosphate-Ca in soils and tissues resulting in low inorganic P that is necessary for its metabolism, but calcifuge and calcicole grasses did not differ much in the ratio of Ca to total P (Zohlen and Tyler, 2004).

The Ca/Mg ratio was one in *P. caudatum* and in *P. aquilinum* (Table 3). Broadley *et al.* (2004) reported a higher Ca/Mg ratio than that found in bracken. They studied 117 species from 24 orders and one unassigned family of angiosperms grown hydroponically and 81 species from 20 orders of angiosperms reported in an ecological survey by Thompson *et al.* (1997). They found that if they excluded seven species from the order Caryophyllales, which have relatively higher Mg contents in their shoots than the other species, Ca and Mg concentration regressed significantly and Ca/Mg ratio was 7.7 g g^{-1} (4.6 mol mol^{-1}).

The differences in Ca/Al and Al/Fe ratios between *P. caudatum* and *P. aquilinum* are remarkable (Table 3) because Al concentration in *P. aquilinum*

in England was low compared to that found in *P. caudatum* in acidic soils, but the concentration of N, P, K, Ca, Mg, Fe, Mn and Cu was higher in *P. aquilinum* shoots. According to Jansen *et al.* (2004) Al accumulators should be defined as plants in which an Al concentration of at least 1000 mg kg^{-1} has been recorded in the dry matter of leaves in at least one specimen growing in its natural habitat. Pinnae of *P. caudatum* only had $152 \text{ mg Al kg}^{-1}$ ($5.62 \text{ mmol kg}^{-1}$) but rhizomes had 1779 mg kg^{-1} ($65.94 \text{ mmol kg}^{-1}$) and roots had 6700 mg kg^{-1} ($248.3 \text{ mmol kg}^{-1}$). *Pteridium* was found not to show Al accumulation in above-ground tissues according to Webb (1954). Based on previous observations by Chenery (1949), Al accumulation is mainly characteristic of some groups belonging to the basal leptosporangiate ferns, including some tree ferns, but largely absent in the more derived ferns (the polypodiaceous ferns) and the heterosporous ferns.

Iron is an essential mineral in plants, but Al is only considered beneficial in some cases (Marschner, 1995). However, several tropical plants, such as *Faramea marginata* (Rubiaceae) are Al accumulators (Britez *et al.*, 2002), with $\text{Ca/Al} < 1$ and $\text{Si/Ca} > 1$. It has been suggested that the formation of an Al-Si complex contributes to the internal detoxification of Al in these plants. Silicon has been reported in bracken (Parry *et al.*, 1985). Hodson *et al.* (2005) reported variation in shoot Si concentration when they compared 735 species, including 59 species of ferns. The relative shoot Si concentration ranged from -2.139 in a Polypodiaceae species to 8.769 in a Poaceae species. They presented relative units originally in percent dry weight. Data were from 125 studies contained in 54 papers and negative relative shoot Si concentration values arise as a consequence of adjusting for between-studies variation during residual maximum likelihood fitting procedures. In ferns Si content was up to 1.352 in a Woodsiaceae species and *P. aquilinum* was 594 in the total of 735 species ranking, with a mean relative shoot Si concentration of 1.299 . In pinnae of *Pteridium caudatum* we found $\text{Ca/Al} = 5 \text{ mol mol}^{-1}$ and the Al concentration was low in comparison with Al accumulators, however Ca/Al is $0.51 \text{ mol mol}^{-1}$ in rhizomes and $0.23 \text{ mol mol}^{-1}$ in roots. The Si content was not measured in *P. caudatum*. A very rough estimate of Si was done by subtracting all the evaluated minerals from the ash mass and Si content was 1.4 times higher in rhizomes than in pinnae.

In *P. caudatum* not only did the roots show high Al concentrations, but also the rhizomes, which are part of the stem, but not of the root system. Liao *et al.* (2004) reported the rhizome of Chinese brake (*Pteris vittata* L.) can be important in the storage of P, Fe and As. They found that in soils with high available As concentrations, such as $1053 \mu\text{g g}^{-1}$, the pinnae and rhizomes had similar concentrations of As, $1386 \pm 161 \mu\text{g g}^{-1}$ and $1217 \pm 96 \mu\text{g g}^{-1}$ respectively, but the As accumulation (concentration \times biomass) was higher in rhizomes than in pinnae because of their higher biomass. However in soils with low available As, $< 1.2 \mu\text{g g}^{-1}$, As concentrations were higher in pinnae than rhizomes.

Pteridium is one of the 85 genera of pteridophytes identified by Page (2004) as having species tolerant of growth on low-nutrient substrates, and he defined

the genus as an ancient living vascular plant (ALVP). According to his study edaphic adaptations enable many ALVPs to continue to exist and to occupy diverse edaphically marginal habitats, in which today, plant competition is necessarily low. The present work suggests that in the acid soils where *P. caudatum* was sampled it concentrates more soluble K than Ca in shoots and rhizomes. This fact probably explains why bracken is used in agriculture as a source of potash (K salts). Both organs have low total Ca and P contents, low water-soluble Ca and Ca bound to oxalate, but a higher fraction of exchangeable Ca and pectate and phosphate bound Ca, which are characteristics of calcifuge grasses that do not change their Ca/P ratio much on calcareous soil or under liming, but reduce their growth on those conditions. Aboveground organs did not show Al accumulation as is common in basal ferns (Chenery, 1949) but a much higher Ca/Al ratio in shoots of *P. caudatum* was observed compared with bracken sampled in temperate regions. Accumulation of Al was found in underground organs, which results in *P. caudatum* contributing this metal to the soil when rhizomes and roots decompose. Plugging this weed is necessary before sowing crops that are not tolerant to Al, not only to prevent the weed from reproducing asexually but also to eliminate the storages of Al in the soil.

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